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(54) Title: MODIFIER TRANSFER FILM AND METHOD OF COOKING A FOOD PRODUCT

(57) Abstract

A film article suitable for cook-in packaging and a method of cooking a food product are described. The film article contains a food-contact layer which includes a copolymer which retains a food product modifier. The copolymer includes substantially water-insoluble segments and substantially hygroscopic segments. The copolymer is capable of transferring at least a portion of the modifier to a food product in contact with the food-contact layer. The film article is particularly well-suited for use as a cook-in film. In this regard, it is capable of sorbing and then transferring a modifier to a packaged food product in sufficient quantity that a separate, post-cooking application of modifier to the food product is unnecessary. Thus, only one package is necessary to cook, ship, and store the food product until it is to be consumed or further processed for retail display. Contamination risks associated with handling and repackaging a cooked food product can be altogether avoided.

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## MODIFIER TRANSFER FILM AND METHOD OF COOKING A FOOD PRODUCT

### BACKGROUND INFORMATION

#### 5 1. Field of the Invention

This invention generally relates to packaging films and to processes employing such films. More specifically, this invention relates to films that can retain and then, during a cook-in process, transfer a modifier to a food product as well as to methods of cooking and transferring a modifier to a food product in  
10 such films.

#### 2. Background of the Invention

Food products often are processed in thermoplastic film packages by subjecting the packaged products to elevated temperatures. For example, such packaged products can be immersed in hot water or placed in a steam-heated  
15 environment. Such thermal processing often is referred to as "cook-in", and films used in such processes are known as cook-in films. The processed and packaged food product can be refrigerated, shipped, and stored until the processed food is to be consumed or, for example, sliced and repackaged into smaller portions for customer display. (Many sliced luncheon meats are processed in this fashion.)  
20 Alternatively, the processed food can be removed immediately from the cook-in package and consumed or further processed for customer display (e.g., sliced and repackaged).

Cook-in films must be capable of withstanding exposure to rather severe temperature conditions for extended periods of time while not compromising their ability to contain the food product. Cook-in processes typically involve a long cook cycle. Submersion in hot water for up to about 4 hours at about 55° to 65°C is common, and submersion in water or steam at 70° to 100°C for up to 12 hours is possible.

Following the cook-in process, the film preferably conforms, if not  
30 completely then at least substantially, to the shape of the contained food product. Often, such conformation is achieved by allowing the film to heat shrink under

cook-in conditions to form a tightly fitting package. In other words, the cook-in film desirably possesses sufficient shrink energy such that the thermal energy used to cook the food product also shrinks the packaging film snugly around the contained product. Alternatively, the cook-in film package can be caused to

5 shrink around the contained food product prior to initiating the cook-in procedure by, for example, placing the package in a heated environment prior to cooking.

The cook-in film also preferably possesses sufficient adherence to the food product to inhibit or prevent "cook-out" during the cook-in process. Cook-out involves the collection of juices (sometimes referred to as "purge") between the

10 surface of the contained food product and the food-contact surface of the packaging material. Preventing cook-out can increase product yield and provide a more aesthetically appealing packaged product.

Often, application of a modifier (i.e., a substance that can change the odor, color, taste, texture, etc., of the packaged product) to the outer surface of a

15 packaged food product is desired. For example, where the food product is poultry or ham, one might wish to impart a smoke color, flavor, and/or odor to the outer surface thereof. This can be accomplished by applying a substance referred to as "liquid smoke" to the outer surface of the food product, normally after the cooking process.

20 Certain characteristics of conventional cook-in films can limit their range of potential uses. For example, many films cannot successfully transfer modifier(s) to a food product during the cook-in process. Previous attempts have been largely unsuccessful, resulting in (at best) non-uniform transfer of modifier. Several explanations have been posited.

25 Merely identifying materials that can sorb and retain a modifier and then, during the cook-in process, transfer the same to a food product has proven problematical. In addition to this selective retention requirement, the ultimate location of the material further complicates the search for prospective candidates. Specifically, such a material necessarily contacts the packaged food product. As

30 such, it must be capable of being formed into the food-contact layer of a cook-in

film, notwithstanding the rather extreme conditions involved in cook-in processes, and providing a sufficient level of adhesion with the packaged food product.

Sufficient adhesion can be a particularly difficult requirement to meet.

Specifically, the film must be able to prevent cook-out and also be removable from the food product once it is cooked. Some presently available cook-in films can prevent cook-out. However, such films tend to adhere to the surface of the food product with such tenacity that portions, or even an entire surface layer, of the food product are torn away when the film is peeled from the food product. As a result, product yield is reduced, and the resulting food product has an unsightly appearance (e.g., a pitted surface).

Because conventional cook-in films have not heretofore successfully transferred modifier to a food product during cook-in, any desired modifier generally must be applied to the food product after the cook-in process. This necessitates stripping the cook-in film from, applying the modifier to the surface of, and then repackaging the cooked food product which adds time, expense, and complexity to the cooking/packaging process. This procedure also increases the likelihood that the food product, which is sterilized by the cooking process, will become contaminated. Eliminating the necessity of removing the food product from its cook-in package, handled, and potentially exposed to microbial contact prior to its consumption or processing for retail display is highly desirable.

Accordingly, a need exists for a cook-in packaging film that can facilitate the transfer of a modifier to a food product during the cook-in process, minimize or prevent cook-out, and yet still peel away from the food product without tearing portions from the surface thereof.

25

## SUMMARY OF THE INVENTION

Briefly, the present invention provides a film article having a food-contact layer that includes a copolymer with a modifier retained therein. The copolymer includes segments that are substantially insoluble in water and other segments that are substantially hygroscopic. The copolymer retains the modifier in such a

manner so that at least a portion of the modifier can be transferred to a food product in contact with the food-contact layer.

- In another aspect, the present invention provides a method of cooking a food product. A food product is enclosed in the above-described film and heated
- 5    so as to at least partially cook the food product. During this cooking process, at least some of the modifier is transferred from the food-contact layer to the food product.

- In yet another aspect, the present invention provides a method for making a multilayer film having a food-contact layer which contains therein a modifier.
- 10    The method includes the step of laminating on a film article a food-contact layer impregnated with a solution including a modifier. Preferably, the food-contact layer includes a copolymer that has substantially water-insoluble segments and substantially hygroscopic segments.

- In a still further aspect, the present invention provides a method for
- 15    impregnating a food-contact layer with a modifier whereby a solution including a modifier is coated on the food-contact layer which retains at least a portion of the modifier. Again, the food-contact layer preferably includes a copolymer that has substantially water-insoluble segments and substantially hygroscopic segments.

- The film article of the present invention is particularly well suited for use
- 20    as a cook-in film. The film is capable of retaining and then transferring a modifier to a packaged food product in sufficient quantity that a separate, post-cooking application of modifier to the food product is unnecessary. This eliminates the contamination risks associated with such an operation. Thus, only one package is necessary to cook, ship, and store the food product until it is to be consumed or
- 25    further processed for retail display.

- Also, the film provides a desirable level of adhesion with the packaged food product. The film adheres sufficiently to the food product during cook-in to minimize or prevent cook-out but still can be peeled from the cooked food product without tearing away a surface layer or portions of the food product. The
- 30    film article also can be made shrinkable and is capable of withstanding the rather severe conditions associated with cook-in procedures.

To assist in understanding the more detailed description of the invention that follows, certain definitions are provided immediately below. These definitions apply hereinthroughout unless a contrary intention is explicitly indicated:

- "polymer" means the polymerization product of one or more monomers and is inclusive of homopolymers, copolymers, terpolymers, 5 tetrapolymers, etc., and blends and modifications of any of the foregoing;
- "mer unit" means that portion of a polymer derived from a single reactant molecule (e.g., a mer unit from ethylene has the general formula —CH<sub>2</sub>CH<sub>2</sub>—);
- 10 "homopolymer" means a polymer consisting essentially of a single type of repeating mer unit;
- "copolymer" means a polymer that includes mer units derived from at least two reactants (normally monomers) and is inclusive of random, block, segmented, graft, etc., copolymers;
- 15 "polyvinyl alcohol", abbreviated herein as "PVOH", means the material formed by partial or complete hydrolysis of poly(vinyl acetate);
- "hydroxy propyl cellulose", abbreviated herein as "HPC", means a thermoplastic, non-ionic cellulose ether formed by the reaction of propylene oxide with alkali cellulose slurried with an aliphatic hydrocarbon and alcohol or propylene oxide;
- 20 "polyolefin" means a polymer in which some of the resulting mer units are derived from an olefinic monomer, which can be linear, branched, cyclic, aliphatic, aromatic, substituted, or unsubstituted (e.g., olefin homo-polymers, copolymers of two or more olefins, copolymers of an olefin and a non-olefinic comonomer such as a vinyl monomer, and the like);
- 25 "(meth)acrylic acid" means acrylic acid and/or methacrylic acid;
- "(meth)acrylate" means acrylate and/or methacrylate;
- "(meth)acrylamide" means acrylamide and methacrylamide;
- "anhydride-modified polymer" means one or more of the following:
- (1) a polymer obtained by copolymerizing an anhydride-containing monomer with a 30 comonomer, (2) an anhydride-grafted copolymer, and (3) a mixture of a polymer and an anhydride-containing compound;

"hygroscopic" means the ability to sorb and retain water (either in liquid or gaseous form) and/or aqueous solutions;

"water insoluble" means the ability to substantially resist dissolution in water and/or aqueous solutions;

5 "free shrink" means the percent dimensional change, as measured by ASTM D 2732, in a 10 cm x 10 cm specimen of film when subjected to heat;

"laminate" means to affix or adhere two or more layers of a film article to one another and can be accomplished by a variety of means including, for example, coextrusion, casting and coating, adhesive bonding, pressure bonding (e.g., via 10 calendering) etc.; and

"cook" means to heat a food product thereby effecting a change in one or more of the physical or chemical properties thereof (e.g., color, texture, taste, and the like).

## 15 DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

Films used in the food packaging industry often are categorized according to the number of layers that make up the film. Some films are made from a single polymer or blend of polymers and thus have only one layer. However, most films include more than one layer and are referred to as multilayer films.

20 In general, the layers of a multilayer film can be classified as "interior" or "exterior". An interior layer is one in which each of the primary surfaces of the layer directly contacts some other layer of the film. In other words, an interior layer is sandwiched by two other layers of the film. On the other hand, an exterior layer is one in which only one of the principal surfaces of the layer is adhered 25 directly to another layer of the film while the other principal surface of each of the two exterior layers forms a principal exterior surface of the film.

If desired, one or more additional interior layers can be included to provide additional or different properties to the film. In addition, any number of tie layers (i.e., internal layers having the primary purpose of adhering two other layers to 30 one another) can be included in the film. Such tie layers can be present primarily on the outside of an interior layer or can be a layer itself. The tie layer preferably

includes modified polyolefin and/or polyurethane, more preferably at least one of modified ethylene/α-olefin copolymer, modified ethylene/unsaturated ester copolymer, and modified ethylene/unsaturated acid copolymer. Anhydride-modified ethylene/α-olefin copolymer and anhydride-modified

- 5       enthylene/unsaturated ester copolymer are particularly preferred. Specific examples include anhydride-grafted linear low density polyethylene (LLDPE) or anhydride-grafted ethylene/vinyl acetate copolymer.

With respect especially to films to be used for cook-in processes, one exterior layer acts as a food-contact layer while the other acts as an outer layer.

- 10      The former serves as the inner layer of a package formed from the film and is in direct contact with the packaged food product. The latter provides abuse resistance by serving as the outer layer of the package, i.e., that layer which is most distant from the food-contact layer.

- To form a multilayer film, the individual layers are laminated, i.e., bonded together. Lamination can be accomplished through the use of adhesives, the application of heat and/or pressure, corona treatment, and even spread or extrusion coating. Lamination also can be accomplished by coextrusion, which involves extruding two or more materials through a single die with two or more orifices arranged so that the extrudates merge and weld together into a laminar structure before cooling. Coextrusion can be employed in film blowing, free film extrusion, and extrusion coating processes.

- Some films, including many which are used in cook-in processes, are oriented prior to use. Orientation involves stretching a film at an elevated temperature (the orientation temperature) followed by setting the film in the stretched configuration (e.g., by cooling). When an unrestrained, unannealed, oriented polymeric film subsequently is heated to its orientation temperature, heat shrinkage occurs and the film returns almost to its original, i.e., pre-oriented, dimensions.

- An oriented film has an orientation which is the multiplication product of the extent to which the film has been expanded in several directions, usually two directions perpendicular to one another. Expansion in the longitudinal direction, sometimes referred to as the machine direction, occurs in the direction the film is formed during

extrusion and/or coating. Expansion in the transverse direction means expansion across the width of the film and is perpendicular to the longitudinal direction.

- Turning now specifically to the film of the present invention, the food-contact layer includes a copolymer having mer units derived from at least two co-reactants. The first co-reactant is capable of homopolymerizing to a material which is substantially water insoluble while the second co-reactant is capable of homopolymerizing to a material which is substantially hygroscopic. In this manner, when the two co-reactants are copolymerized (by any suitable copolymerization technique known in the art), the resultant copolymer is believed to contain two distinct types blocks or segments, some of which provide water insolubility and other which provide hygroscopicity to the polymer. The two types of segments function both interdependently, in that they are inseparable parts of the same polymer, and independently, in that they provide the polymer of the food-contact layer with water insolubility and hygroscopicity. This is highly advantageous for the several reasons.

- The hygroscopic, i.e., water sorbing or swellable, segments of the copolymer sorb and retain at least some of a modifier, particularly aqueous modifiers, i.e., those which are suspended or dissolved in an aqueous carrier, when the modifier is brought into intimate contact therewith. (Of course, where the modifier is not aqueous in nature, the water-insoluble segments can provide the desired sorption and retention. Also, where the modifier is, for example, an emulsion, both types of segments can be involved in sorption and retention.) Subsequently, when the food-contact layer is brought into contact with a food product, at least a portion of the modifier transfers from the copolymer to the food product. Although such transfer most readily occurs during the cook-in process, cook-in is not required to effect transfer.

- The water-insoluble segments of the copolymer prevent the food-contact layer from being solubilized by the food product during and after cook-in and do not themselves dissolve or solvate in the aqueous modifier. In this regard, the water-insoluble segments serve to anchor the hygroscopic portions to the rest of

the copolymer and thereby maintain the integrity of the food-contact layer during cook-in.

Thus, a copolymer including both water-insoluble and hygroscopic segments advantageously (1) allows for sorption and subsequent transfer (to a food product during cook-in) of a modifier, and (2) remains intact (or at least substantially intact) so that the food-contact layer can be separated from the food product at any desired time after cooking.

The relative amounts of water-insoluble and hygroscopic segments in the copolymer can be selected to provide any desired balance of water insolubility and hygroscopicity. Generally, the water-insoluble segments can be present in the copolymer at a weight percentage ranging from about 1 to about 99 while the hygroscopic portions can be present at a weight percentage ranging from about 99 to about 1; more preferably, the water-insoluble segments can be present at a weight percentage ranging from about 20 to about 95 while the hygroscopic segments can be present at a weight percentage ranging from about 80 to about 5; most preferably, the water-insoluble portions can be present at a weight percentage ranging from about 40 to about 90 while the hygroscopic portions can be present at a weight percentage ranging from about 60 to about 10.

Preferably, the water-insoluble segments of the copolymer have a solubility in an aqueous medium of less than 10%, more preferably less than 5%, more preferably still less than 1%, even more preferably less than 0.1%, yet more preferably less than 0.05%, more preferably still less than 0.01%, even more preferably less than 0.005%, and most preferably less than 0.001%. (All of the foregoing percentages are weight percentages.) The water-insoluble segments preferably are derived from one or more of amides, olefins, esters, alkyl (meth)acrylates, vinylics, dienes, alkynes, lactides, sulfides, sulfones, urethanes, siloxanes, and silanes. Of the foregoing, amides, olefins, and esters are particularly preferred, with amides such as nylon 6, nylon 6/6, nylon 12, nylon 6/12, and the like being most preferred.

The hygroscopic segments of the copolymer preferably have a water sorption capacity of greater than 5%, more preferably greater than 10%, more

preferably still greater than 20%, even more preferably greater than 30%, yet more preferably greater than 40%, even more preferably still greater than 50%, yet more preferably still greater than 100%, still more preferably greater than 500%, even more preferably greater than 1000%, and most preferably greater than 5000%.

- 5 All of the foregoing percentages are weight percentages.

Preferably, the hygroscopic segments are at least somewhat water soluble.

The hygroscopic segments preferably have a solubility parameter greater than 9 (g/cc)<sup>1/2</sup>, more preferably greater than 12 (g/cc)<sup>1/2</sup>, and even more preferably greater than 14 (g/cc)<sup>1/2</sup>.

- 10 The substantially hygroscopic segments preferably are derived from one or more of ethers, celluloses, saccharides, anhydrides, caprolactones, imines, (meth)acrylic acid, (meth)acrylamides (such as, for example, N,N-dimethylacrylamide, N-isopropylacrylamide, etc.), cinnamides (such as, for example, N-(meth)acrylylglycinnamide), succinimides (e.g., N-vinylsuccinamic acid), piperidines (such as, for example, N,N-dimethyl-3,5-methylenepiperidinium chloride, 2-vinylpiperidine, 4-vinylpiperidine, and the like), vinyl acetates, vinyl pyrrolidones, vinyloxazolidones (such as, for example, vinylmethyloxazolidone), sulfonic acids (such as, for example, 2-methacryloyloxyethane-1-sulfonic acid, 3-methacryloyloxypropane-1-sulfonic acid, 3-(vinyloxy)propane-1-sulfonic acid, and the like), phosphoric acids, phosphonic acids (e.g., ethylenephosphonic acid), silicic acids, vinylamines (such as, for example, 2-vinylpyridine, 4-vinylpyridine, and the like), vinyl sulfuric acids (e.g., 4-vinylphenyl sulfuric acid), benzoic acids (e.g., 4-vinylbenzoic acid as well as derivatives such as 4-vinylbenzyltrimethylammonium salt), maleic acid, and phenols (e.g., 4-vinylphenol). Of the foregoing, ethers are preferred. Hygroscopic segments derived from one or more of ethylene glycol, propylene glycol, and tetramethylene glycol are particularly preferred.

- From the foregoing description of preferred water insoluble and hygroscopic reactants, one can see that a particularly preferred copolymer is one which includes mer units derived from esters and mer units derived from amides, i.e., an ether/amide copolymer which is the polymerization product of (at least) an ether compound and an amide compound. The amide and ether portions can be present in the copolymer in

any desired amount depending upon the particular application for which the film article is to be used. The copolymer can include between about 1 to 99 weight percent mer units derived from an ether and between about 99 to 1 weight percent mer units derived from an amide. Preferably, however, the copolymer includes between 5 about 20 to 80 weight percent mer units derived from an ether and between about 80 to 20 weight percent mer units derived from an amide.

A particularly preferred type of ether/amide copolymer is a block copolymer, i.e., poly(ether block amide) (PEBA). This type of block copolymer can be produced from a molten state polycondensation of a dicarboxylic 10 polyamide and a polyether diol. Preferred PEBA's include PEBAX<sup>TM</sup> MX 1074 and 6031 (Elf-Atochem North America, Inc.; Philadelphia, PA), both of which contain blocks of nylon 12 and poly(ethylene glycol).

In accordance with another embodiment of the invention, the food-contact layer can include HPC or a blend of HPC and another polymer. Commercially 15 available HPCs include Klucel<sup>TM</sup> (Aqualon Division of Hercules, Inc.; Wilmington, Del.) and Nisso<sup>TM</sup> resins (Nippon Soda Co. Ltd.; Tokyo, Japan).

Chemical or radiative crosslinking of the HPC to an extent sufficient to render the food-contact layer substantially water insoluble is preferred. In this manner, the HPC food-contact layer remains intact and does not dissolve into the 20 food product. Preferred chemical crosslinking agents include, e.g., aldehydes, diisocyanates, glyoxal, boric acid, and sodium borate. Radiative crosslinking means are well known to those of ordinary skill in the art.

In general, the food-contact layer can have a thickness ranging from about 0.25 to 250  $\mu\text{m}$  (0.01 to 10 mils), preferably from 1.3 to 25  $\mu\text{m}$  (0.05 to 1 mil), more 25 preferably from 2.5 to 13  $\mu\text{m}$  (0.1 to 0.5 mils), and most preferably from about 5 to 7.5  $\mu\text{m}$  (about 0.2 to 0.3 mils).

To withstand cook-in time and temperature conditions, the polymer(s) from which the food-contact layer is formed preferably has/have a melting point ranging from about 70° to 250°C, more preferably from about 85° to 230°C, even more 30 preferably from about 100° to 200°C, and most preferably from about 120° to 180°C.

Other polymers optionally can be blended with the materials described above for the food-contact layer to obtain either a diluted effect or a synergistic effect. Thus, other moisture absorbing polymers or relatively water-insoluble polymers can be blended with any of the polymers or copolymers described above to form the food-contact layer. The blend can include any desired amount of additional polymer.

Suitable water-insoluble polymers include polyolefins, polyamides, polyesters, etc., with polyamides being preferred. Suitable moisture absorbing polymers can include one or more of the following water-soluble polymers: poly(ethylene imine), poly(acrylic acid), polyacrylamide, poly(methacrylic acid), polymethacrylamide,

10 poly(N,N-dimethylacrylamide), poly(N-isopropylacrylamide), poly(N-(meth)acrylylglycinnamide), poly(vinyl acetate), polyvinylpyrrolidones, polyvinyloxazolidone, polyvinylmethyloxazolidone, poly(ethylene sulfonic acid), poly(phosphoric acid), poly(silicic acid), poly(styrenesulfonic acid), polyvinylamine, poly(2-vinylpyridine), poly(4-vinylpyridine), poly(vinyl sulfuric acid), poly(vinyl alcohol-co-vinyl sulfuric acid), poly(N,N-dimethyl-3,5-methylenepiperidinium chloride), poly(ethylene phosphonic acid), poly(maleic acid), poly(2-methacryloyloxyethane-1-sulfonic acid), poly(3-methacryloyloxypropane-1-sulfonic acid), poly(4-vinylbenzoic acid), poly(4-vinylbenzyltrimethylammonium salts), poly[3-(vinyloxy)propane-1-sulfonic acid], poly(4-vinylphenol), poly(4-vinylphenyl sulfuric acid), poly(2-vinylpiperidine), poly(4-vinylpiperidine), and poly(N-vinylsuccinamic acid). In some circumstances, forming the food-contact layer solely from one or more of the foregoing moisture absorbing polymers might be possible.

Advantageously, the food-contact layer of the film article of the present invention not only can transfer modifier to a packaged food product but also can provide purge resistance, i.e., inhibit or prevent cook-out during the cook-in process. This is a significant advantage, especially where the food product is meat, poultry, or fish. Preferably, the film article results in less than 20 weight percent cook-out, i.e., less than 20% (by wt.) of the original weight of the food product is lost as purge. More preferably, the film article results in less than 10% cook-out, even more preferably less than 5%, more preferably still less than 2% cook-out, and most preferably less than 1% cook-out.

To assist in reducing or eliminating cook-out, a food-contact layer having a surface energy of greater than 34 dynes/cm, preferably greater than 38 dynes/cm, more preferably greater than 42 dynes/cm, even more preferably greater than 46 dynes/cm, and most preferably greater than 50 dynes/cm is preferred. At such 5 surface energies, the food-contact layer is believed to provide sufficient adhesion with the food product to prevent or substantially minimize cook-out.

If the film adheres so strongly to the cooked food product such that it cannot be peeled therefrom without tearing away portions of the same, the copolymer of the food-contact layer can be blended with one or more polymers 10 that lower its adhesion. In this regard, less polar polymers such as polyolefins having a surface energy of about 36 dynes/cm or less can provide beneficial results. On the other hand, if adhesion between the film article and food product is too low, the surface energy of the food-contact layer can be increased. This can be accomplished by, for example, subjecting the surface of the food-contact layer 15 to sufficient energetic radiation (i.e., of sufficiently high intensity or for a sufficiently long period of time) to achieve a desired increase in surface energy. Examples of radiative techniques include plasma and corona treatments.

Alternatively, the surface energy of the food-contact layer can be increased by including one or more polar additives such as polyesters, polyamides, polylactic 20 acid, and polar polyolefins such as ethylene/unsaturated acid copolymers, modified polyolefins, and blends thereof.

When formed into a food-contact layer, PEBA advantageously has been found to provide sufficient adhesion with a packaged food product during cook-in to substantially prevent cook-out without the need for corona treatment. At the 25 same time, adhesion between PEBA and the food product is sufficiently low that the film article can be peeled from the food product after cook-in without substantial tearing of particles from the food product.

As mentioned previously, modifiers are substances that can change the odor, color, taste, texture, etc., of a packaged product. Normally, the modifier 30 effects a change in the surface of the product to which it is applied when sorbed by that surface. This sorption can occur either without, but preferably with (in the

case of meat, poultry, or fish), a concurrent cook-in process. Any desired modifier(s) can be included in the food-contact layer, especially those that are dissolved or suspended in an aqueous medium. Non-limiting examples include colorants (e.g., dyes or pigments such as  $\beta$ -carotene), odorants, flavorants, 5 antioxidants (to control rancidity), antimicrobial agents, enzymes, odor absorbents, or blends of any of the foregoing materials. Modifiers which impart more than one of the above properties also can be used. An example of a modifier commonly used in the packaged food industry is "liquid smoke", a substance derived from wood and capable of being sorbed (i.e., absorbed or adsorbed) by a 10 food product such as, for example, beef, mutton, poultry, fish, cheese, and the like. Liquid smoke is a colorant-flavorant-odorant which imparts a wood-smoked quality to red meat, poultry, ham, sausage, etc. Various liquid smoke compounds, as well as the other modifiers listed above, are available from a number of different commercial sources.

15 The modifier can be sorbed into the food-contact layer either during or after production of the film article, e.g., by adding modifier to the pelletized or molten resin which will form the food-contact layer prior to extrusion or coextrusion thereof. Preferably, sorption of the modifier takes place after the film article has been made. This can be accomplished by any suitable means whereby a 20 modifier or modifier solution is brought into contact with the food-contact layer for a time sufficient to allow the food-contact layer to sorb a desired amount of modifier. Where the film article is in the form of a flat sheet, it can simply be immersed in a bath of a modifier or a solution that includes a modifier so as to impregnate the food-contact layer with modifier. This can be done as a batch or 25 continuous process. Where the film is in the form of a tube with the food-contact layer on the inner surface thereof, the modifier can be contacted with the tube inner surface and sorbed thereby. This can be accomplished in a number of ways such as, for example, by introducing a slug of modifier solution at a low position within a vertically oriented section of tube in the tube processing system, with a 30 nip roll as a liquid seal at the lower end, and then passing the tube through the stationary slug. See, e.g., U.S. Pat. No. 2,901,358. Where the film article is

- fabricated into a bag, the modifier can be added by simply filling the bag or, as disclosed in U.S. Pat. No. 5,484,001, partially filling the bag and then squeezing the modifier between a moveable external roller and backing plate so that it is dispersed along and absorbed into a desired portion of the inside (i.e., food-contact layer) of the bag. Other means for sorbing the modifier into the food-contact layer include soaking the food-contact layer in a modifier or modifier mixture and then laminating it to the rest of the film structure; coating a modifier solution onto the food-contact layer by means of, for example, a flexographic printing press, a doctor blade, gravure coating, reverse roll coating, etc.; or
- 5 spraying a modifier solution into the inside of a tube or bag formed from the film article.
- 10

Surprisingly, the food-contact layer of the film article of the present invention has been found to be capable of sorbing, retaining, and then transferring a relatively large amount of modifier as a percentage of the total weight of the food-contact layer. For example, a multilayer film having a PEBA food-contact layer that constitutes approximately 10% of the film's total weight and thickness, can sorb and retain between about 50 and 250 weight percent of a liquid smoke modifier, based on the total weight of the multilayer film. If expressed as a percentage of the weight of the PEBA layer alone, the sorption ranges from about

15

20 500 to 2500 weight percent. The amount of modifier retained by the food-contact layer often can vary with the viscosity of the modifier. Generally, lower viscosity modifiers are sorbed and retained to a greater degree than higher viscosity modifiers.

The values provided in the foregoing paragraph are based on the amount of modifier retained by the food-contact layer shortly after soaking the film article in a liquid smoke solution, i.e., with little or no drying of the film article. However, where a film article is allowed to dry (e.g., at room temperature for a period of 12 to 18 hours), the amount of liquid smoke modifier retained by the food-contact layer is somewhat lower. For a multilayer film having a PEBA food-contact layer, the amount of modifier retained after drying ranges from about 20

25

to 75 weight percent, based on the total weight of the film, or about 200 to 750 weight percent, based on the weight of the PEBA layer alone.

The foregoing sorption percentages are illustrative only. Depending upon a particular set of circumstances (e.g., the type of modifier, the composition of the food-contact layer, cook-in conditions, etc.), observed values can be higher or lower. Actual sorption values can vary from 0.1 to 10,000 weight percent but generally range between 0.5 to 1000, or even 1 to 500, weight percent.

The degree of sorption also can vary somewhat depending on the amount of time that the food-contact layer is exposed to the modifier as well as the temperature maintained during the sorption process. The values reported above are based on soak times ranging from 30 seconds to 10 minutes. (Generally, most sorption occurs within about 2 minutes of the time that soaking is initiated.) Where the modifier is liquid smoke compound, sorption times can range from seconds to several hours, e.g., 5 seconds to 24 hours. Preferred sorption times range from about 30 seconds to 30 minutes, more preferably from about 1 to about 10 minutes, most preferably from about 2 to about 5 minutes. As illustrated in the Examples below, the film articles of the present invention advantageously provide adequate sorption of liquid smoke within about 1 to 10 minutes.

Sorption temperatures generally range from about 0° to 70°C, with a temperature range of about 10° to 30°C being more preferred. Depending on the circumstances, higher or lower temperatures also can be employed.

The food-contact layer preferably transfers at least 1% (by wt.), more preferably at least 5% (by wt.), even more preferably at least 10% (by wt.), more preferably still at least 20% (by wt.), even more preferably at least 30% (by wt.), yet more preferably at least 40% (by wt.), and most preferably at least 50% (by wt.) of the modifier retained therein is transferred to a food product packaged within the film article. In general, a greater proportion of the retained modifier is transferred to the food product where a food product is cooked and packaged within the film article than where an already cooked food product is simply packaged within the film article. About 45 to 95% (by wt.) of a liquid smoke

modifier retained in the food-contact layer of a film article of the present invention is believed to be transferred to a food product cooked in the film article.

The film article of the present invention can have a single layer or include a number of layers. Preferably, the film article is a multilayer film having an outer

- 5 layer comprising at least one of polyolefin, polystyrene, polyamide, polyester, poly(ethylene/vinyl alcohol), polyvinylidene chloride, polyether, polyurethane, and polycarbonate. The outer layer preferably provides abuse resistance to the film article when it is formed into a cook-in package. Polyolefins and/or polyamides often prove to be particularly useful in this regard.

- 10 Suitable polyolefins include polyethylene homopolymer or copolymer, polypropylene homopolymer or copolymer, and polybutene homopolymer or copolymer. Preferred examples include ethylene/α-olefin copolymer, propylene/α-olefin copolymer, butene/α-olefin copolymer, ethylene/unsaturated ester copolymer, and ethylene/unsaturated acid copolymer. Specific  
15 examples of preferred polyolefins include one or more of LLDPE, ethylene/vinyl acetate copolymer (EVA), propylene/ethylene copolymer, and propylene/butene copolymer. An ethylene/α-olefin copolymer includes mer units derived from ethylene and from one or more C<sub>3</sub> to C<sub>20</sub> α-olefins such as 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene, and the like. The resulting polymer  
20 molecules include long chains with relatively few side chain branches and the side branching that is present is short compared to non-linear polyethylenes (e.g., low density polyethylene homopolymer). Ethylene/α-olefin copolymers generally have a density in the range of from about 0.86 g/cc to about 0.94 g/cc. LLDPE generally is understood to include that group of ethylene/α-olefin copolymers  
25 which fall into the density range of about 0.915 to about 0.94 g/cc. Sometimes, linear polyethylene having densities of from about 0.926 to about 0.94 are referred to as linear medium density polyethylene (LMDPE). Lower density ethylene/α-olefin copolymers can be referred to as very low density polyethylene (VLDPE, typically used to refer to ethylene/butene copolymers available from Union  
30 Carbide with a density ranging from about 0.88 to about 0.91 g/cc ) and ultra-low

density polyethylene (ULDPE, typically used to refer to ethylene/octene copolymers supplied by Dow Chemical Co.).

Ethylene/α-olefin copolymers also include homogeneous polymers such as metallocene catalyzed EXACT™ linear homogeneous ethylene/α-olefin

- 5      copolymers (Exxon Chemical Co.; Baytown, Texas); TAFMER™ linear homogeneous ethylene/α-olefin copolymers (Mitsui Petrochemical Corp.; Tokyo, Japan); and AFFINITY™ long-chain, branched homogeneous ethylene/α-olefin copolymers (Dow Chemical Co.; Midland, Michigan). Homogeneous polymers have relatively narrow molecular weight and composition distributions.
- 10     Homogeneous polymers are structurally different from heterogeneous polymers (e.g., ULDPE, VLDPE, LLDPE, and LMDPE) in that homogeneous polymers exhibit a relatively even sequencing of comonomers within a chain, a mirroring of sequence distribution in all chains, and a similarity of length of all chains, i.e., a narrower molecular weight distribution. Furthermore, homogeneous polymers are
- 15     typically prepared using single-site type catalysts (e.g., metallocenes) rather than Ziegler-Natta catalysts. Such single site catalysts typically have only one type of catalytic site, which is believed to be the basis for the homogeneity of the polymers produced thereby.

- 20     Suitable polyamides from which the outer layer can be formed include one or more of the following: polyamide (i.e., nylon) 6, polyamide 66, polyamide 9, polyamide 10, polyamide 11, polyamide 12, polyamide 69, polyamide 610, polyamide 612, polyamide 61, polyamide 6T, polyamide MXD6, and copolymers thereof. More preferably, the polyamide is selected from the group consisting of polyamide 6, polyamide 66 and polyamide 6/66. Even more preferably, the
- 25     polyamide in the outer layer comprises a blend of polyamide 6, 66 or 6/66 with a second polyamide having a different crystalline structure from the first polyamide, including one or more of the following: polyamide 6, polyamide 66, polyamide 9, polyamide 10, polyamide 11, polyamide 12, polyamide 69, polyamide 610, polyamide 612, polyamide 61, polyamide 6T, polyamide MXD6, and copolymers
- 30     thereof.

If the outer layer comprises polyamide, adding polymers that are compatible with the polyamide or polyamide blend so as to modify the properties of the polyamide can be beneficial for some applications. Suitable polymers include polyolefins, such as those incorporating acids, esters, anhydrides or salts of carboxylic acids; and polar, non-polyolefinic materials such as polyesters, EVA, etc.

- 5 If desired, additional layers can be included as interior layers. Preferred materials from which such interior layers can be formed include polyolefin, particularly EVA, ethylene/alkyl acrylate copolymer (e.g., ethylene/methyl acrylate, ethylene/ethyl acrylate, ethylene/butyl acrylate, etc.), LDPE, and 10 ethylene/α-olefin copolymer (e.g., LLDPE or VLDPE); polyamide; polyurethane; and blends of any of the foregoing. In addition, any of the materials described above as suitable for use in the outer layer also can be used to form one or more interior layers.

- 15 If desired, the film article can contain an interior layer that acts as a barrier. (Barrier layers inhibit the transmission of one or more gases, e.g., O<sub>2</sub>.) Such a layer can be advantageous for extending the shelf-life of an oxygen-sensitive product, such as beef, poultry, pork, or fish, when packaged in the film article of the present invention. Such an oxygen barrier layer preferably is formed from at 20 least one material selected from the group consisting of ethylene/vinyl alcohol copolymer, vinylidene chloride copolymer, polyamide, PVOH, polyhydroxyaminoether, polyalkylene carbonate, or a blend of any of the foregoing. If desired, oxygen barrier functionality also or alternatively can be provided by appropriate material selection for the outer layer or other interior 25 layers.

Each of the foregoing materials from which the film article can be constructed are commercially available from a number of suppliers. Specific examples are listed in the Examples below.

- 30 If heat shrinkable, the film article preferably has a free shrink at 85°C (185°F), determined according to ASTM D 2732, of from about 5 to 70%, more preferably from about 10 to 50%, and most preferably from about 15 to 35% in at

least one direction (i.e., the longitudinal (L) or transverse (T) directions).

Preferably, the film article is biaxially oriented, and preferably the film has a free shrink at 85°C of at least 10%, more preferably at least 15%, in each direction in each direction (L and T). Preferably, the film article has a total free shrink (L+T)

5 of from about 30 to 50% at 85°C. The film preferably is stretched in both the L and T directions at ratios ranging from about 1:1.5 to 1:7 and, more preferably, from about 1:2 to 1:4. Stretch orienting in the L and T directions can be followed by rapid quenching to lock in the molecular orientation. The resulting film article is an oriented film which is heat shrinkable, preferably at the conditions at which  
10 the cook-in procedure is performed.

Alternatively, the oriented film article can be heat-set. Heat-setting can be done at a temperature from about 60° to 200°C, more preferably from about 70° to 150°C, and even more preferably from about 80° to 90°C.

In general, the film article of the present invention can have any total thickness  
15 desired, as long as the film provides the desired properties for the particular packaging operation in which it is used. Preferably, the film article has a total thickness (i.e., a combined thickness of all layers) of from about 13 to 250 µm (0.5 to 10 mils), more preferably from about 25 to 130 µm (1 to 5 mils), and still more preferably from about 50 to 75 µm (2 to 3 mils).

20 The film article preferably has a Young's modulus ranging from about 34 to 3400 MPa (5,000 to 500,000 psi), more preferably from about 70 to 2100 MPa (10,000 to 300,000 psi), and most preferably from about 280 to 1400 MPa (40,000 to 200,000 psi). The food-contact layer itself can have a Young's modulus ranging from about 20 to 3400 MPa (3,000 to 500,000 psi).

25 Preferably, the material from which the food-contact layer is formed has a melt flow index ranging from about 0.1 to 1,000 g/10 minutes, more preferably from about 0.5 to 500 g/10 minutes, and most preferably from about 1 to 50 g/10 minutes (ASTM D-1238; 235°C/1 kg).

Illustrated below are preferred examples of film structures in accordance with  
30 the present invention. In each of these structures, the following abbreviations are used:

FC: food-contact layer, as described above;

PA: polyamide-containing layer, preferably having a thickness of from 2.5 to 130  $\mu\text{m}$  (0.1 to 5 mils), more preferably from 5 to 75  $\mu\text{m}$  (0.2 to 3 mils), most preferably from 13 to 25  $\mu\text{m}$  (0.5 to 1 mils);

5 PO: polyolefin-containing layer, preferably having a thickness of from 2.5 to 130  $\mu\text{m}$  (0.1 to 5 mils), more preferably from 5 to 75  $\mu\text{m}$  (0.2 to 3 mils), most preferably from 13 to 25  $\mu\text{m}$  (0.5 to 1 mils);

10 B: oxygen barrier layer, preferably having a thickness of from 0.25 to 130  $\mu\text{m}$  (0.01 to 5 mils), more preferably from 1.3 to 13  $\mu\text{m}$  (0.05 to 0.5 mils), most preferably from 2.5 to 7.5  $\mu\text{m}$  (0.1 to 0.3 mils); and

15 TIE: tie layer having a preferred thickness of 0.25 to 25  $\mu\text{m}$  (0.01 to 1 mils), more preferably 1.3 to 13  $\mu\text{m}$  (0.05 to 0.5 mils), most preferably 2.5 to 7.5  $\mu\text{m}$  (0.1 to 0.3 mils).

In the following film structures, the individual layers are shown in the order in which  
15 they would appear in the film:

	FC (monolayer)
	FC / PA
	FC / PO
	FC / TIE / PO
20	FC / B / PA
	FC / TIE / PA
	FC / PO / PA
	FC / B / PO
	FC / TIE / B / PO
25	FC / TIE / B / TIE / PO
	FC / PA / B / PA
	FC / TIE / PO / TIE / PA
	FC / TIE / B / TIE / PA
	FC / TIE / PA / TIE / PA
30	FC / TIE / B / PA / TIE / PA

## FC / TIE / PO / TIE / B / PA / TIE / PO

These representative film structures are intended to be illustrative only and not limiting in scope.

The film article of the present invention can be produced by any suitable technique known in the art of film making, such as, for example, coextrusion, extrusion coating, or lamination. Coextrusion is preferred.

- If desired, the film article can be chemically or radiatively crosslinked. When electronically crosslinked, the film is subjected to an energetic radiation treatment, such as high energy electron treatment, which induces crosslinking of molecules of the irradiated material. The irradiation of polymeric films is disclosed in U.S. Patent No. 4,064,296 (Bornstein et al.) incorporated herein in its entirety by reference thereto. Bornstein et al. discloses the use of ionizing radiation for crosslinking the polymer present in the film. Radiation dosages often are expressed in terms of the radiation unit "RAD", megarads (MR), or kiloGrays (kGy), with one MR being equivalent to 10 kGy. A suitable radiation dosage of high energy electrons is in the range of from about 16 to 166 kGy, more preferably from about 44 to 139 kGy, and still more preferably from about 50 to 80 kGy. Preferably, irradiation is carried out by an electron accelerator with the dosage level being determined by standard dosimetry methods.
- In carrying out a cook-in process in accordance with the present invention, a food product is enclosed in a film article as described above, with the food-contact layer being in contact with the food product. Any suitable means of enclosing the food product in the film article can be employed. Preferably, the film article is in the form of a bag or casing with a single opening. Such a bag or casing can be formed by, e.g., heat sealing one end of a length of tubular film or by sealing both ends of the tube and then slitting one edge to form the bag mouth. Where the film article is made in the form of flat sheets, bags can be formed therefrom by heat-sealing three edges of two superimposed sheets of film. That the food-contact layer be capable of being heat-sealed to itself is preferred.
- PEBA, as well as HPC, are heat-sealable in this manner.

The food product is placed inside of the bag or casing and the opening is sealed closed, e.g., by heat-sealing or clipping, so that the resultant enclosure is substantially liquid-tight. The enclosed food product is then heated for a time and at a temperature sufficient to at least partially, but preferably fully, cook the food product. During this process, at least some of the modifier retained within the food-contact layer is transferred to the food product. Any suitable means of heating can be employed, including immersing the enclosed food product in a bath of heated water or steam, or placing the enclosed food product in a hot air or steam cabinet. In one preferred embodiment, the film article is heat shrinkable so that the food-contact layer will be in close contact with the food product, thereby facilitating transfer of the modifier. If the film is not heat shrinkable, the inside of the bag or casing can be evacuated and collapsed against the food product prior to sealing the bag or casing closed.

After the desired degree of cooking has been achieved, the processed and packaged food product is removed from the heating means and allowed to cool. The film article can be stripped from the food product at any desired time after the cooking process has been completed. That is, the film article immediately can be stripped and the food product then can be either consumed or further processed, e.g., sliced and repackaged into smaller portions for customer display by a retailer. Alternatively, the processed and packaged food product can be refrigerated, shipped to a retailer, and stored until the processed food is to be consumed or further processed as described above.

Food products which can be packaged and cooked in accordance with the present invention can be any of those foods which are amenable to cook-in packaging, including whole muscle or chopped red meat, poultry, pork, or fish. Also included are foods which are not intended to be cooked-in but simply stored within the package, during which time a modifier is to be transferred to the packaged food product. Such foods include cheese, vegetables, fruits, and already cooked meat, poultry, pork, or fish. In general, however, the invention is most advantageous when used as a cook-in package for, e.g., poultry, ham, beef, lamb,

goat, horse, fish, liver sausage, mortadella, and bologna; more preferably, poultry, ham, beef and bologna; even more preferably, poultry and ham.

The invention will now be described with reference to the following examples, which are intended to be illustrative only and not limiting in scope.

5

## EXAMPLES

### Example 1

A 6-layer film in accordance with the present invention was prepared. The structure of the film was

- 10 FC / I / TIE / B / TIE / O  
wherein FC represents a 38 µm (1.5 mils) thick food-contact layer of PEBA<sup>TM</sup>  
MX 1074 poly(ether block amide) copolymer; I represents a 76 µm (3.0 mils)  
thick internal layer made from a blend of TYMOR<sup>TM</sup> 1203 anhydride-grafted  
LLDPE (Morton International; Chicago, IL) and EXACT<sup>TM</sup> 4011 homogeneous  
15 ethylene/α-olefin copolymer (Exxon Chemical Co.; Baytown, TX); each TIE  
represents a 28 µm (1.1 mils) thick tie layer of TYMOR<sup>TM</sup> 1203 anhydride-grafted  
LLDPE; B represents a 28 µm (1.1 mils) thick oxygen barrier layer of EVAL<sup>TM</sup>  
LC-E105A ethylene/vinyl alcohol copolymer (Eval Co. of America; Lisle, IL); and  
O represents a 190 µm (7.5 mils) thick outer layer made from a blend of PE  
20 5269T<sup>TM</sup> ethylene/vinyl acetate copolymer (Chevron Chemical Co.; Houston, TX) and  
FORTIFLEX<sup>TM</sup> J60-500C-147 high density polyethylene (Solvay Polymers, Inc.;  
Deer Park, TX).

- This film was prepared by coextruding each polymer (or polymer blend) at  
between 193° and 277°C (380° and 530°F) through a circular die held at a  
25 temperature of approximately 216°C (420°F). The extruded tube of film was  
cooled with water and flattened to a width of about 6 cm. The flattened film was  
passed through the scanned beam of an electronic crosslinking unit where it  
received a total dosage of about 105 kGy. After irradiation, the flattened tube was  
passed through hot water having a temperature of from about 97° to 99°C (206°  
30 to 210°F), inflated into a bubble, and oriented to result in a tube of oriented film,

the tube having a lay flat width of about 16.5 cm (6.5 in.), with the multilayer film having a total thickness of 56  $\mu\text{m}$  (2.2 mils).

The resulting film had about 20% free shrink in the longitudinal direction and about 30% free shrink in the transverse direction when immersed in hot water  
5 at 85°C (185°F) using ASTM method D 2732-83.

#### Example 2

Multilayer films made according to the teaching of Example 1 and monolayer PVOH films were subjected to cook-in testing by soaking

10 15 cm  $\times$  15 cm (6 in.  $\times$  6 in.) film samples in a Charsol Select™ 24 liquid smoke solution having a pH of 2.4 (Red Arrow Products Co., Inc., Manitowoc, WI) for a predetermined period of time ranging from 1 to 10 minutes to allow the PEBA or PVOH food-contact layer to sorb some of the liquid smoke. Some of the samples were simply shaken dry and then weighed to determine the amount of liquid smoke  
15 absorbed by the food-contact layer. Others were allowed to dry for at least 12 hours before weighing. This was done to replicate actual use conditions where, in some instances, the food-contact layer is impregnated with modifier shortly before packaging a food product (and will therefore be wet with modifier solution during the transfer of the modifier to the food product) and in other instances the  
20 modifier-soaked food-contact layer is dried by the time a food product is packaged in the film article.

A chicken breast emulsion having 3% salt, 0.5% phosphate, and 35% water, the balance being defatted chicken breast meat (all percentages based on the total weight of chicken breast), was prepared. Sections of 10 cm (4 in.)  
25 diameter poly(vinyl chloride) pipe were stuffed with the chicken breast emulsion and capped on one end with a 15 cm  $\times$  15 cm sample of liquid smoke-impregnated film. The other end was capped with a control film having a food-contact layer comprising a 50:50 blend of nylon 12 and nylon 6/12. The control film did not contain modifier but was used as a basis for comparison of the meat-adhesion/cook-out prevention capabilities of the films of the present invention.  
30

Restraining plates were placed over the capped ends of the stuffed pipe sections, and the resultant sample assemblies were subjected to a cook-in procedure wherein the sample assemblies were immersed in a hot water bath at 60°C (140°F) for 30 minutes, 65°C (149°F) for an additional 30 minutes, and then 5 70°C (158°F) for a final 30 minutes. The sample assemblies then were chilled in an ice bath until cool, at which time the restraining plates were removed.

Each of the tested film samples were inspected visually for their ability to prevent cook-out. This was done by noting the extent to which any purge was trapped between the surface of the cooked chicken and the film. The samples then 10 were peeled from the cooked chicken. During this procedure, the degree to which the food-contact layer of the film samples adhered to the surface of the chicken also was noted, in terms of the ability of the film to prevent cook-out by strong adherence with the chicken and also in terms of the ability of the film to release from the chicken without tearing away a surface layer or pieces therefrom. After 15 the films were removed, the chicken was examined to determine the extent to which the food-contact layer transferred liquid smoke to the chicken during the cook-in process.

The test results are summarized in Tables 1 and 2, wherein each value is an average from three identically tested samples. Table 1 sets forth the test results 20 for film samples (identified according to their respective food-contact layers) which were allowed to dry for at least 12 hours after soaking in liquid smoke before initiating the cook-in procedure described above.

Table 1

	PEBA	PEBA	PVOH-1 <sup>a</sup>	PVOH-2 <sup>b</sup>
Soak time (min)	1	10	1	5
Initial film wt. (g)	9.35	9.65	1.65	1.72
Dry film wt. <sup>c</sup> (g)	12.19	12.39	4.28	5.55
Modifier sorbed <sup>d</sup> (wt. %)	30.4	28.4	159	222
Adhesion <sup>e</sup>	moderate	moderate	low	low
Transfer <sup>f</sup>	good	good	good	good

- a) M1030 PVOH (Mono-Sol Division of Chris-Craft, Inc.; Gary, Indiana)
- b) M1040 PVOH (Mono-Sol Division of Chris-Craft, Inc.)
- 5 c) The weight of the film after being dried for at least twelve hours after being soaked in a liquid smoke solution.
- d) The amount of modifier retained by the food-contact layer expressed as a percentage of the initial, pre-soaked weight of the film.
- 10 e) A qualitative measure of the degree to which the food-contact layer adhered to the surface of the cooked chicken product and prevented cook-out. "Very high" represents essentially no cook-out but substantial tearing of chicken upon removal of the film; "high" represents essentially no cook-out and only some tearing of chicken upon removal of the film; "moderate" represents little or no cook-out and no tearing of chicken upon removal of the film; "low" represents some cook-out and no tearing; and "none" indicates no adhesion with substantial cook-out. The comparative film having a blend of nylon 6 and nylon 6/12 for the food-contact layer exhibited "very high" to "high" adhesion under this rating system.
- 15 f) A qualitative measure of the degree to which the food-contact layer transferred liquid smoke to the chicken. "Good" indicates a high degree, "fair" indicates a moderate degree, and "poor" indicates a low degree of transfer.
- 20

Table 2 sets forth test results for films samples which had not been dried prior to commencement of the cook-in procedure.

Table 2

	PEBA	PEBA	PVOH-1 <sup>a</sup>	PVOH-2 <sup>b</sup>
Soak time (min)	1	10	1	10
Initial film wt. (g)	3.20	2.80	1.23	1.25
Wet film wt. <sup>c</sup> (g)	6.04	5.5	5.36	4.84
Modifier sorbed (wt. %)	89	96	336	287
Adhesion	moderate	moderate	low	low
Transfer	good	good	good	good

a) Same as in Table 1.

b) Same as in Table 1.

5 c) The weight of the film immediately after soaking, with excess liquid smoke having been only shaken off of the film.

The data of Tables 1 and 2 show that films of the present invention exhibit a high degree of modifier absorption and transfer. In addition, the films provide a  
10 desirable balance of food adhesion, i.e., cook-out is substantially prevented but removal of the film does not result in tearing of chicken particles.

With respect to the films having a PEBA food contact layer, the percent absorption in Tables 1 and 2 is expressed as a percentage of the entire film weight. In such films, the PEBA-containing food-contact layer accounted for  
15 approximately 10% of the total weight and thickness of the film. Thus, the amount of liquid smoke absorbed by the PEBA as a percentage of the weight of the PEBA alone is much higher than the values reported in Tables 1 and 2.

### Example 3

20 Films made according to the procedure set forth in Example 1 (i.e., having a PEBA food-contact layer) were formed into casings, weighed, filled with a liquid smoke solution, and allowed to soak for about 10 minutes. The casings then were drained and allowed to dry for at least 12 hours before being reweighed to determine the amount of liquid smoke absorbed by the food-contact layer.

The casings were stuffed with a meat emulsion consisting of about 30-45% boneless, skinless turkey breast, 50-65% water, 2% NaCl, 0.5% sodium tripolyphosphate, 2% carrageenan, and 1% tapioca starch (all percentages being weight percentages). These stuffed casings were clipped to form a substantially liquid-tight enclosure and placed in a high-humidity thermal processing unit to cook the meat emulsion. Cooking temperatures ranged from 60° to 82°C (140° to 180°F).

The meat emulsions were weighed before and after cooking to determine the amount purge loss (i.e., cook-out) resulting from the cook-in process. After cooking, the stuffed casings were chilled and then the casings were stripped from the cooked meat product. Observations were made regarding meat adhesion, modifier transfer, and color uniformity of the surface of the modified and cooked meat product.

The test results are summarized in Table 3, wherein each value is an average from three identically-tested samples.

Table 3

	LS-1 <sup>a</sup>	LS-2 <sup>b</sup>	LS-3 <sup>c</sup>
Initial casing wt. (g)	9.28	9.64	9.09
Final casing wt. <sup>d</sup> (g)	11.75	12.20	12.12
Modifier sorbed (wt. %)	26.6	26.6	33.3
Initial meat wt. (kg)	1.12	1.13	1.06
Cooked meat wt. (kg)	1.10	1.13	1.05
Percent cook-out <sup>e</sup>	1.2	0.4	0.85
Adhesion	low/none	low/none	low
Transfer	good	good	fair
Uniformity <sup>f</sup>	mottled	uniform	uniform

- a) LFBN Liquid Smoke having a pH of 6.1 (Red Arrow Products Co.)
- 20 b) N52 Liquid Smoke having a pH of 5.4 (Red Arrow Products Co.)
- c) Select 55 Liquid Smoke having a pH of 5.5 (Red Arrow Products Co.)

- d) The weight of the casing after soaking in the liquid smoke solution and then drying for at least 12 hours.
  - c) Weight percentage of purge which collected between the meat and the casing, expressed as a weight percentage of the initial (i.e., pre-cooked) weight of the meat.
- 5      f) A qualitative measure of the degree to which liquid smoke color uniformly transferred to the surface of the meat product, ranging from "uniform" (high degree of uniformity) to "mottled" (non-uniform transfer of modifier leading to a mottled or blotchy surface appearance).
- 10     This data from Table 3 show that films of the present invention can reduce cook-out to levels of approximately 1% or less. Further, the films provide good absorption and subsequent transfer of modifier.

#### Example 4

15     A film was made as in Example 1 but, instead of a food-contact layer formed from PEBA<sup>X</sup>™ MX 1074, the food-contact layer was formed from PEBA<sup>X</sup>™ 6031 (Elf-Atochem). The film was subjected to cook-in testing as described in Example 2 and exhibited "fair" modifier transfer and "high" adhesion, as those terms are defined above.

20     

#### Example 5

A monolayer film of Klucel™ HPC (Aqualon Division of Hercules, Inc.) was subjected to cook-in testing as described in Example 2. The film exhibited "good" and "uniform" modifier transfer, and "low" adhesion, as those terms are defined above.

25     While the invention has been described with reference to illustrative examples, those skilled in the art will understand that various modifications can be made to the invention as described without departing from the scope of the claims  
30     which follow.

That which is claimed is:

1. A film article comprising a food-contact layer, said food-contact layer comprising:
  - 5 a) a copolymer comprising substantially water-insoluble segments and substantially hygroscopic segments; and
  - b) a modifier retained by said copolymer,  
at least a portion of said modifier being capable of transferring from said copolymer to a food product in contact with said food-contact layer.
- 10 2. The film article of claim 1 wherein said substantially water-insoluble segments are derived from one or more of amides, olefins, esters, alkyl (meth)acrylates, vinylics, dienes, alkynes, lactides, sulfides, sulfones, urethanes, siloxanes, and silanes.
- 15 3. The film article of claim 2 wherein at least some of said substantially water-insoluble segments are derived from one or more of an amide, an olefin, and an ester.
- 20 4. The film article of claim 3 wherein at least some of said substantially water-insoluble segments are derived from an amide.
5. The film article of claim 4 wherein said amide is one or more of nylon 6, nylon 12, nylon 6/6, and nylon 6/12.
- 25 6. The film article of claim 1 wherein said substantially hygroscopic segments are derived from one or more of ethers, cellulosics, saccharides, anhydrides, caprolactones, imines, (meth)acrylic acid, (meth)acrylamides, cinnamides, succinimides, piperidines, vinyl acetates, vinylpyrrolidones, vinyloxazolidones, sulfonic acids, phosphoric acids, phosphonic acids, silicic acids, vinylamines, vinyl sulfuric acids, maleic acid, benzoic acids, and phenols.
- 30 7. The film article of claim 8 wherein at least some of said substantially hygroscopic segments are derived from an ether.

8. The film article of claim 1 wherein said copolymer comprises mer units derived from one or more ethers and from one or more amides.

5 9. The film article of claim 8 wherein said copolymer comprises blocks of ether and amide segments.

10 10. The film article of claim 1 wherein said modifier comprises a colorant, odorant, flavorant, antioxidant, antimicrobial agent, enzyme, odor absorbent, or a blend of any of the foregoing.

11. The film article of claim 1 wherein said modifier is a liquid smoke compound.

15 12. The film article of claim 1 further comprising an outer layer.

13. The film article of claim 12 wherein said outer layer comprises a polyolefin, polystyrene, polyamide, polyester, ethylene/vinyl alcohol copolymer, polyvinylidene chloride, polyether, polyurethane, or polycarbonate.

20 14. The film article of claim 12 further comprising at least one interior layer positioned between said food-contact layer and said outer layer, said interior layer comprising a polyolefin, polyamide, or polyurethane.

25 15. The film article of claim 12 further comprising an interior layer positioned between said food-contact layer and said outer layer, said interior layer comprising an ethylene/vinyl alcohol copolymer, polyvinylidene chloride, polyamide, polyvinyl alcohol, polyhydroxyaminoether, or polyalkylene carbonate.

30 16. A package made from the film article of claim 1.

17. A method of cooking a food product, said method comprising the step of sufficiently heating a food product enclosed in the film article of claim 1 so

as to at least partially cook said food product, whereby at least some of said modifier is transferred from said food-contact layer to said food product.

18. A method for making a multilayer film having a food-contact layer  
5 which contains therein a modifier, said method comprising the step of laminating  
on a film article a food-contact layer impregnated with a solution comprising a  
modifier.

19. A method for impregnating a food-contact layer with a modifier, said  
10 method comprising the step of coating a solution comprising a modifier onto said  
food-contact layer so that at least a portion of said modifier is retained by said  
food-contact layer.

# INTERNATIONAL SEARCH REPORT

Intern. Appl. No  
PCT/US 97/05418

**A. CLASSIFICATION OF SUBJECT MATTER**  
**IPC 6 B65D81/34 B65D65/40 B32B27/08 A22C13/00**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
**IPC 6 B65D B32B A22C**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 473 091 A (VISKASE CORP) 4 March 1992 see page 3, line 16 - page 4, line 11; examples ---	1,18,19
A	US 4 250 199 A (UNDERWOOD GARY L ET AL) 10 February 1981 see column 2, line 11 - line 32; examples ---	1
A	US 5 384 170 A (BASTIOLI CATIA ET AL) 24 January 1995 see claims; examples ---	1
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	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

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PCT/US 97/05418

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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